AD-A202 291

APPLICATION OF NONDESTRUCTIVE EVALUATIONS TO THE PREDICTION OF TURBINE FUEL PEROXIDATION POTENTIAL

FINAL REPORT
No. SwRI-7958-840

By

G.E. Fodor
K.B. Kohl
D.W. Naegeli
Fuels and Lubricants Research Division
Southwest Research Institute
San Antonio, Texas
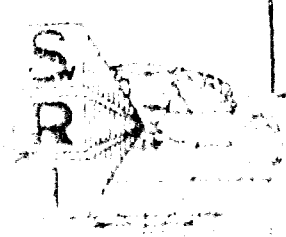
Prepared for

Naval Research Laboratory
Washington, D.C.

DTIC
ELECTE
NOV 2 3 1988
H

January 1988

88 1122 008

SOUTHWEST RESEARCH INSTITUTE
HOUSTON

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified		1b. RESTRICTIVE MARKINGS	
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for Public Release; Distribution Unlimited	
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE			
4. PERFORMING ORGANIZATION REPORT NUMBER(S) 17-7958-840		5. MONITORING ORGANIZATION REPORT NUMBER(S)	
6a. NAME OF PERFORMING ORGANIZATION NTIAC Southwest Research Institute	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Naval Research Laboratory	
6c. ADDRESS (City, State, and ZIP Code) P.O. Drawer 28510 San Antonio, TX 78284		7b. ADDRESS (City, State, and ZIP Code) Washington, DC 20375-5000	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Defense Logistics Agency	8b. OFFICE SYMBOL (If applicable) DTIC-DF	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER DLA900-84-C-0910, CLIN 0001BJ	

8c. ADDRESS (City, State, and ZIP Code) DTIC Cameron Station Alexandria, VA 22314	10. SOURCE OF FUNDING NUMBERS			
	PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.

11. TITLE (Include Security Classification)

Application of Nondestructive Evaluations to the Prediction of Turbine Fuel Peroxidation Potential

12. PERSONAL AUTHOR(S)
G.E. Fodor, K.B. Kohl, and D.W. Naegeli

13a. TYPE OF REPORT Final	13b. TIME COVERED FROM 8/5/87 TO 2/5/88	14. DATE OF REPORT (Year, Month, Day) February 1988	15. PAGE COUNT 15

16. SUPPLEMENTARY NOTATION

Performed as a Special Task for the Nondestructive Testing Information Analysis Center

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Nondestructive Evaluation, Turbine Fuel, Peroxidation, Infrared Spectra, Fuel Storage .

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

After the theoretical and experimental baselines were established to determine the potential peroxide content of jet fuels, nondestructive methods of analyses were evaluated to augment the procedures.

The use of proton nuclear magnetic resonance (NMR), ultraviolet (UV), and infrared (IR) spectroscopies were evaluated. UV and NMR did not respond to the trace-quantity compositional changes caused by autoxidation in the examined fuels. Direct detection and measurement of the primary autoxidation intermediates, that is, peroxides and hydroperoxides, were not feasible by the applied nondestructive analytical methods. Indications are that IR may be used for the detection and measurement of peroxide decomposition products such as alcohols and carbonyl compounds.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT [X] UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. D.R. Hardy		22b. TELEPHONE (Include Area Code) (202) 767-3555	22c. OFFICE SYMBOL Code 6180

DD FORM 1473, 84 MAR   83 APR edition may be used until exhausted. All other editions are obsolete.

I. BACKGROUND

Between 1962 and 1983, both the U.S. Navy and some commercial air carriers experienced fuel system failures in jet aircraft flying in the Western Pacific. It was shown by Shertzer (1)* and Hazlett (2) that these difficulties correlated with peroxides in the fuel. The peroxides attacked the neoprene, nitrile, and Buna-N diaphragms and O-rings used in the fuel systems of turbine engines. It was also shown that fuel peroxidation is indicative of fuel degradation. While chemical methods are available for the measurement of existing peroxide concentrations, the potential tendency of a fuel to develop excessive concentrations of peroxides after lengthy storage periods could not be predicted with methodology prior to this study.

II. OBJECTIVE

The objective of this study was to establish background information and methodology that could be used as a basis for a nondestructive testing support to predict the peroxidation potential of turbine fuels.

III. APPROACH

The theoretical and experimental baselines have already been established for the methodology to determine the potential peroxide content of kerosenes.(3,4) In that work, it was shown that (a) the square root of the peroxide concentration was proportional to the stress duration, and (b) the rate of formation of peroxides was strongly temperature dependent, but, above a minimum value, it was independent of the partial pressure of oxygen. The work also showed that the strong correlation of the global oxidation rate constants with temperature in the Arrhenius plot gave no evidence for a change in the reaction mechanism over the temperature range from 43° to $120^{\circ}C$ for the six fuels studied in that program.

The usefulness of various nondestructive instrumental methods, such as ultraviolet (UV), infrared (IR), and nuclear magnetic resonance (NMR) spectroscopies was evaluated as aids in further developing the methodology. Results of the spectroscopic investigations were compared to those of the peroxide determinations.

---

* Underscored numbers in parentheses refer to references at the end of this report.

IV. EXPERIMENTAL DESIGN

Experiments were performed on two relatively unstable kerosenes, fuel Nos. 15708 and 16581. Baseline peroxidation experiments were carried out on both fuels in an atmosphere of air in a 43°C long-term storage in amber borosilicate bottles. Oxidation experiments were also carried out in two independent, nominally identical, pressurized stainless steel reactors under 240 kPa of oxygen at 80°, 100°, and 120°C. Each experiment was carried out in replicate, where the average number of individual runs was six.

V. ANALYSES OF FUEL SAMPLES

Analyses of the fuel samples included the measurement of peroxides, gum, water, and acid numbers. In the bottle storage experiments, oxygen concentrations were also determined in both the liquid and vapor phases by gas chromatography. Monitoring of the oxygen concentrations was necessary to assure that oxidations would not become oxygen concentration limited. To assure the presence of adequate oxygen concentrations, the oxygen contents of the vapor phases were maintained above 10 vol%. For brevity, only the pertinent peroxide concentrations are discussed in this report.

Both the base fuels and their oxidized products were examined by infrared, ultraviolet, and proton nuclear magnetic resonance spectroscopies. Analyses of the two fuels by UV and NMR did not reflect any measurable changes as a result of their oxidation, probably due to the relatively low sensitivity of these methods. However, the infrared spectra showed some distinct absorptions that reflected the presence of oxidation products. Characteristic vibrations in the infrared spectrum that are assigned to alkyl peroxides center around 820 to 890 cm^{-1}, while aryl peroxides absorb near 1000 cm^{-1}. If the peroxide contains structures with the elements of CO-O-O-CO, then its IR spectrum will resemble that of an anhydride, with the characteristic splitting of the band. The dialkyl and diaryl peroxides absorb in the region of 1790 and 1815 cm^{-1} and 1770 and 1800 cm^{-1}, respectively, i.e., in the same general region where carbonyl bond absorptions take place.(5)

Infrared analyses showed three frequency regions that changed during oxidation. These frequencies, centered at around 3400-, 1740-, and 1300 cm^{-1}, are usually assigned to O-H, C=O, and possibly C-O stretching vibrations. The multiplicity of bands between

1650 and 1800 cm^{-1} may indicate the presence of peroxides; however, no clear indication of the presence of peroxides was found between 820 to 890 cm^{-1}. At this time, it is uncertain if the peak(s) centered around 1740 cm^{-1} are due to carbonyl or peroxide absorptions. Later discussions will offer possible assignments.

VI. RESULTS AND DISCUSSION

A. Peroxide Formation at 43°C in Bottle Storage Experiments

As a baseline for the elevated temperature oxidation reactions, relatively low temperature long-term storage experiments were performed at 43°C. Due to the limited duration of the project, these experiments were carried out only to 18 weeks, corresponding to about 12 to 18 months of storage at normal ambient conditions. Infrared spectra of the oxidized and unoxidized (fresh) fuels were superimposable, and their differential spectra were without features. This fact is probably due to the limited resolution of IR. In 18 weeks at 43°C, the peroxide contents increased from zero to 53.3 and 10.9 ppm for fuel Nos. 15708 and 16581, respectively. These data are graphically illustrated in Fig. 1, which is presented in accordance with the findings described by
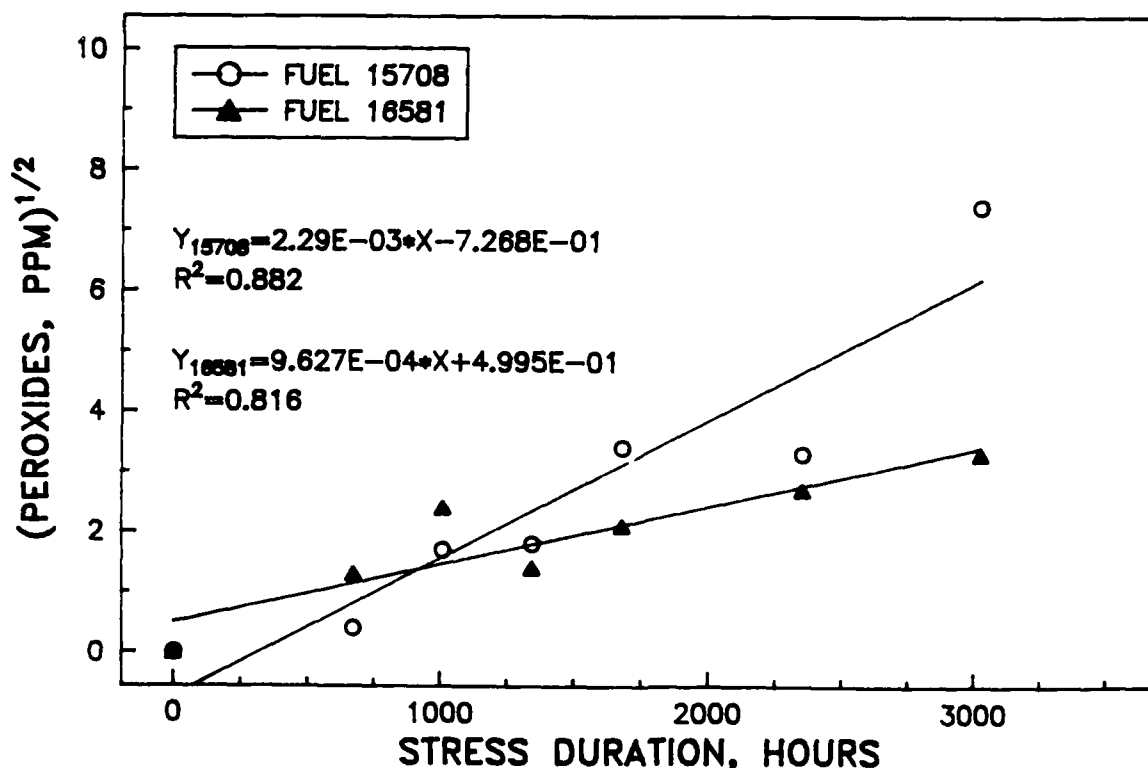
Figure 1. <u>Oxidation of fuels at 43°C bottle storage</u>

3

A-1

Fodor, Naegeli, et al. (Ref. 3, 4), where the square roots of the peroxide concentrations (in ppm) are plotted against the stress periods, expressed in hours. Linear regression constants and the linear correlation coefficients, R^2 values, are also given on the figure.

The slopes of the curves shown in Fig. 1 represent global rate constants for peroxide formation. If the rate of peroxide decomposition in the fuel is neglected, the global rate constant is basically the rate of oxidation.

B.   Peroxide Formation During Elevated Temperature Experiments

In two nominally identical stainless steel reactors, both fuels (Nos. 15708 and 16581) were oxidized under a constant 240 kPa of oxygen at 80°, 100°, and 120°C for various time periods. Each experiment was performed in replicate, numbering between 2 to 14 individual runs.

The average data generated during the oxidation of fuel No. 15708 are shown in Fig. 2. The results show that the correlation of the square root of the peroxide concentration with stress duration continues to be favorable under each stress temperature studied. Additionally, Fig. 2 shows the corresponding linear regression constants and coefficients. It may be noted that this fuel exhibits an induction period lasting for about 30 hours at 80°C. The global rate of oxidation increased so rapidly at 100° and 120°C that, for practical purposes, the induction periods disappeared at these temperatures.

Fig. 3 shows the results obtained in oxidizing fuel No. 16581. In contrast to fuel No. 15708, this fuel shows induction periods at both 80° and 100°C, indicating that this fuel is more stable than fuel No. 15708. This conclusion is the same as that suggested by the 43°C bottle storage experiments.

Since the global autoxidation rate constants have not yet been determined at a sufficient number of temperatures for each of the respective induction and post induction periods, only a fragmentary Arrhenius plot could be constructed; this is presented in Fig. 4.

4
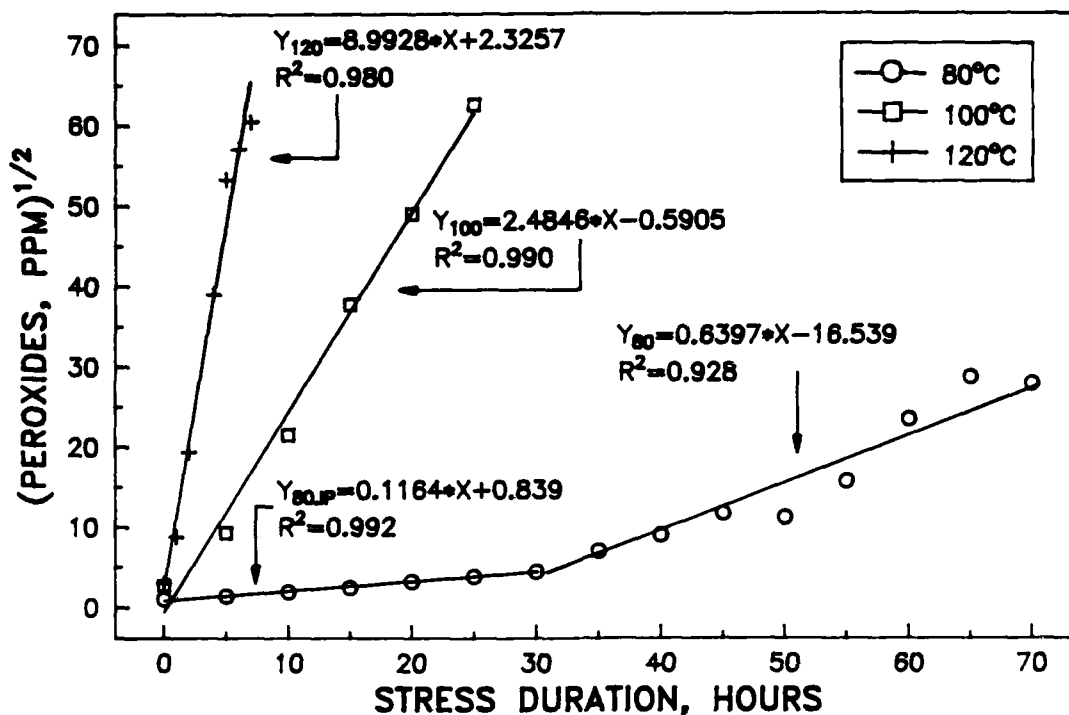
Figure 2. Oxidation of fuel No. 15708, 240 kPa oxygen
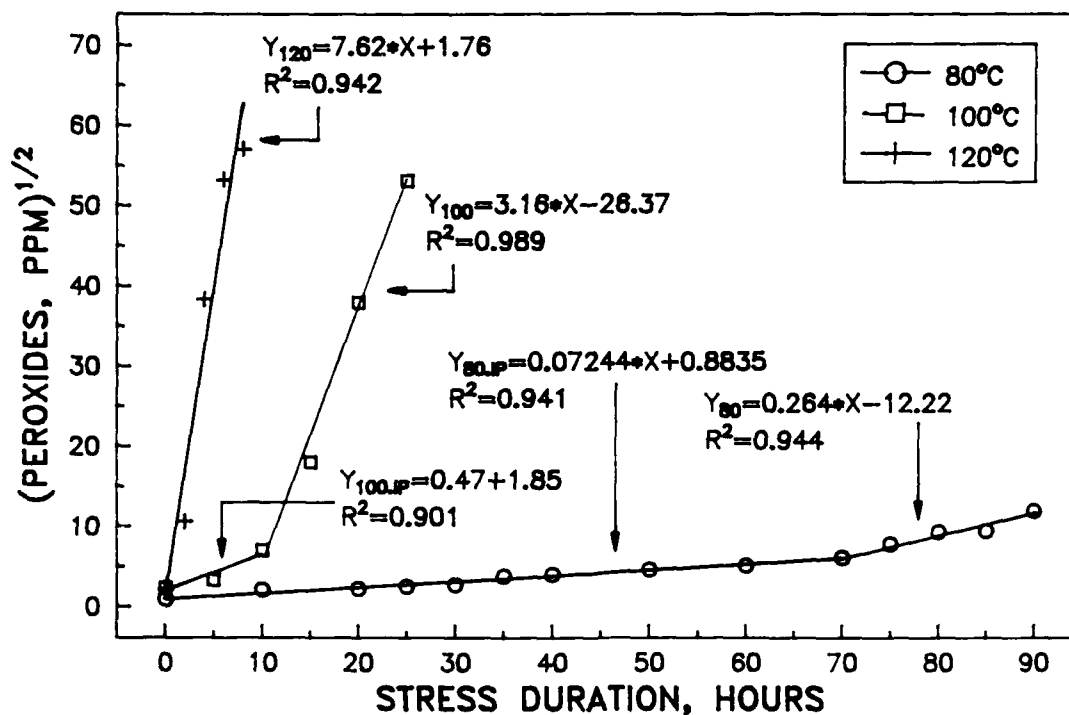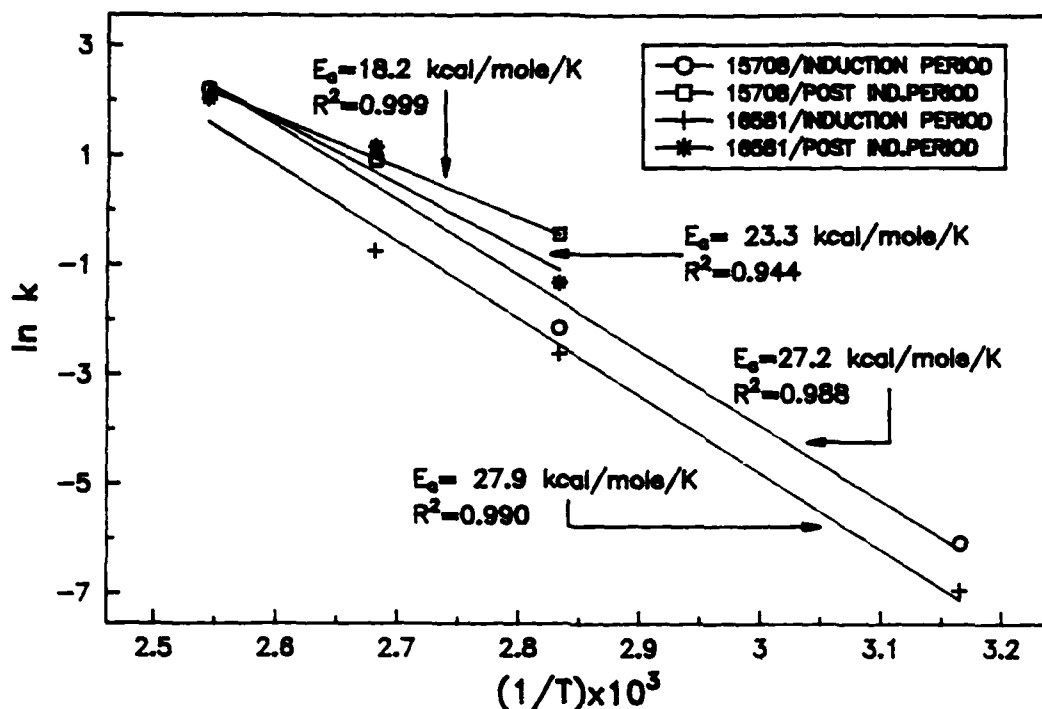

Figure 3. Oxidation of fuel No. 16581, 240 kPa oxygen

Figure 4. Arrhenius plot of fuel Nos. 15708 and 16581, oxidation (peroxide data)

C. Infrared Analysis of Turbine Fuel Oxidation

The fuel samples that yielded the previously discussed peroxide concentrations were also analyzed by infrared spectrophotometry. Infrared spectra were obtained from the fresh (unoxidized) fuels and from their oxidized products. From these spectra, computer-generated differential IR spectra were obtained. To illustrate, Figs. 5 through 10 depict the new, an oxidized, and differential IR spectra of fuel Nos. 15708 and 16581. From the differential IR spectra, absorbance values were calculated at frequencies centered at approximately 3400, 1740, and 1300 cm^{-1}. Data scatter, or error, was calculated from standard deviation and average data. It ranged between 5 and 18 percent and was similar in magnitude to the error expected by ASTM D 3703, "Standard Test Method for Peroxide Number of Aviation Turbine Fuels." Due to the relatively weak IR response of the oxidized samples from the 80°C experiments even after 70 hours of stress, these data were considered unreliable; therefore, they were not used in this report.

Time dependence of differential IR absorbance for the oxidations of fuel No. 15708 at 100°C is shown in Fig. 11. These data describe the increase in band intensities centered at frequencies around 3400, 1740, and 1300 cm^{-1}. Corresponding data for the same fuel

6
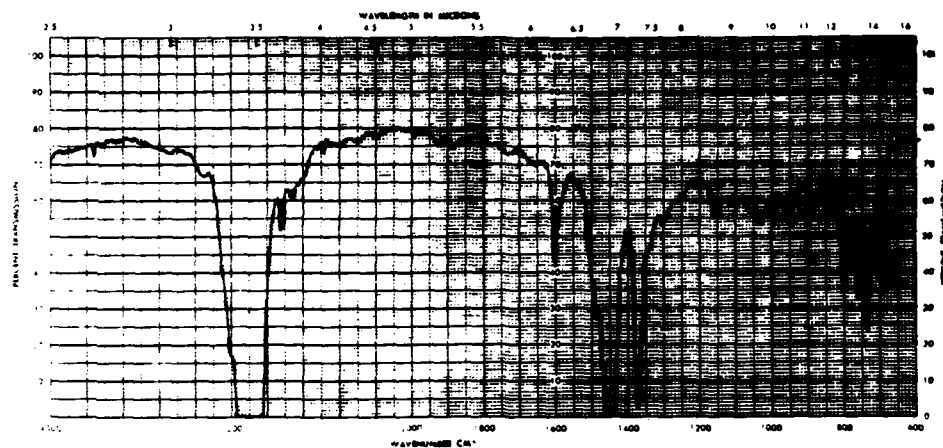
Figure 5. Infrared spectrum of neat fuel No. 15708
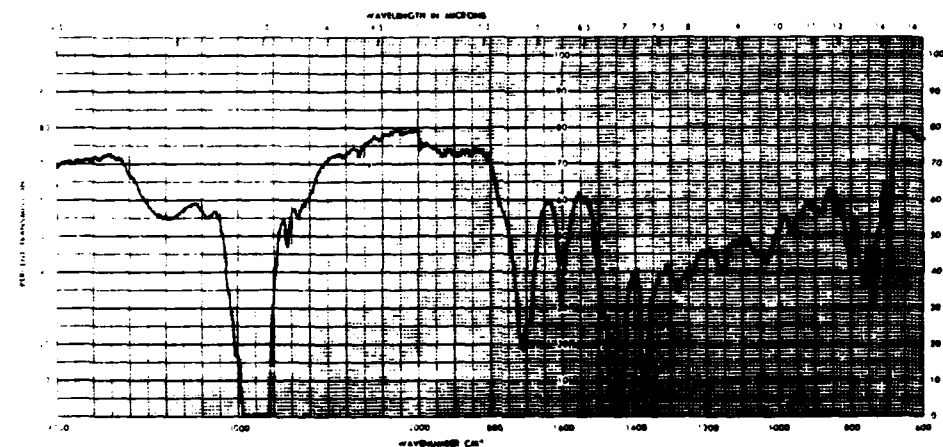
Figure 6. Infrared spectrum of oxidized fuel No. 15708
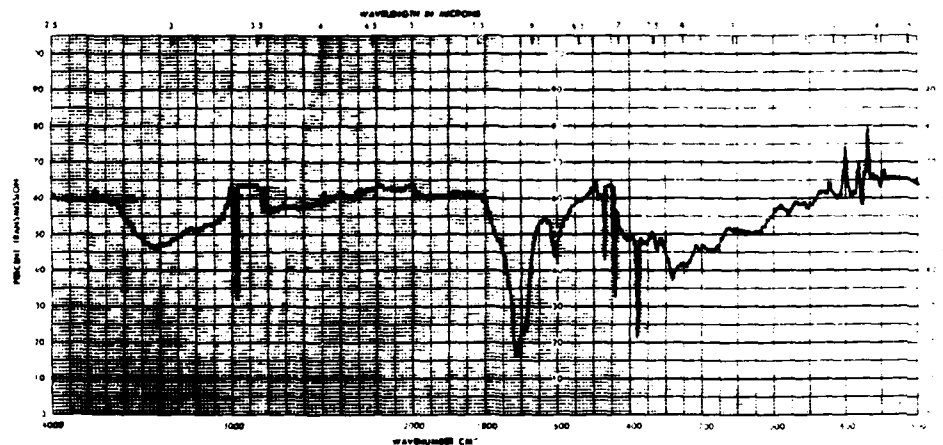
Figure 7. Differential infrared spectrum of fuel No. 15708

7
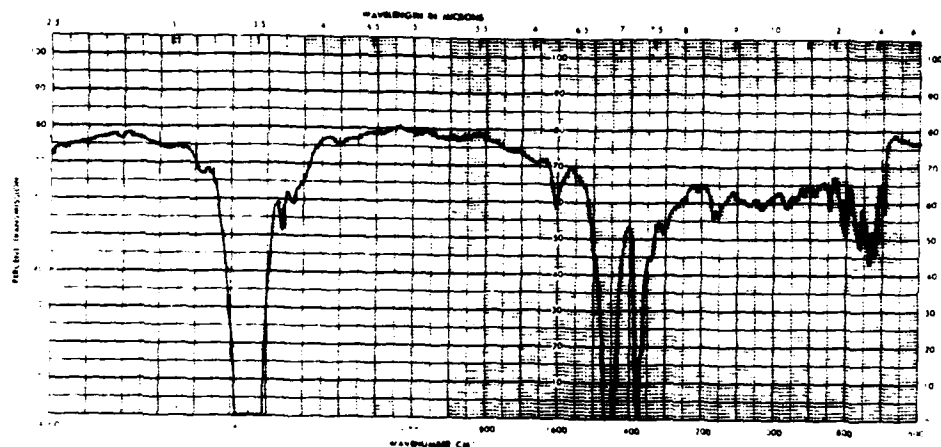
Figure 8. Infrared spectrum of neat fuel No. 16581
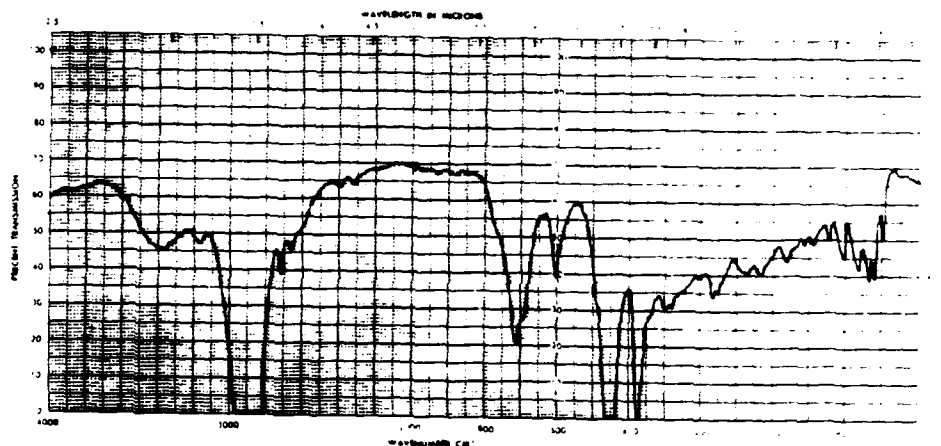
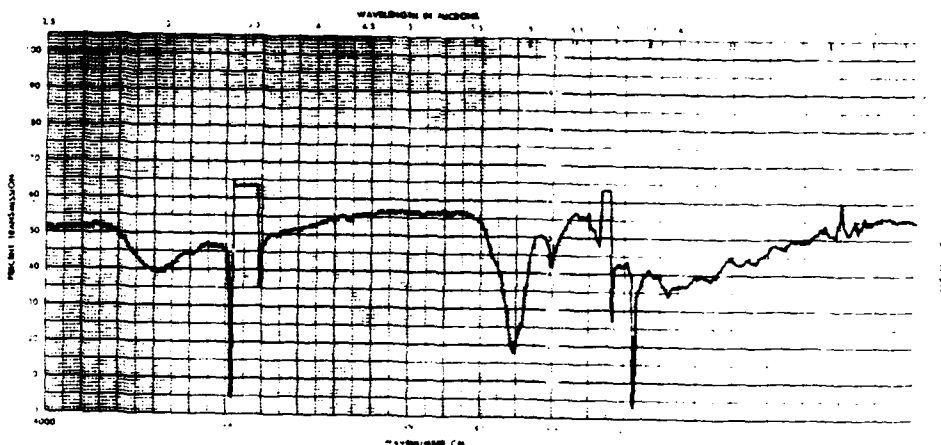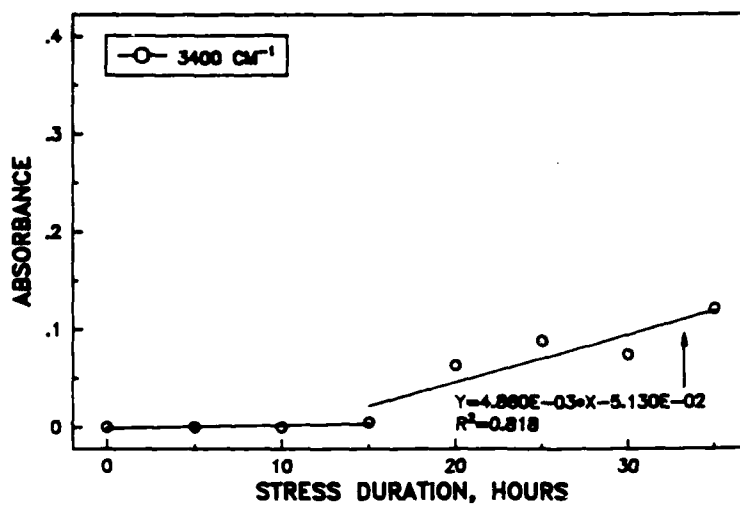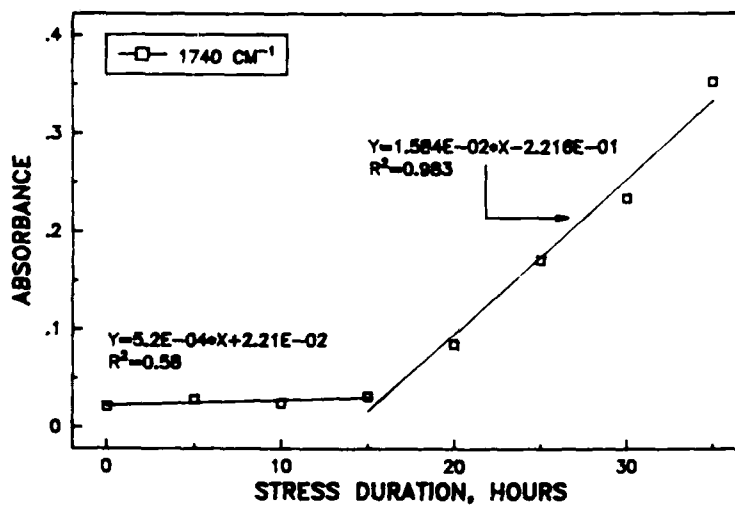**Figure 9.** Infrared spectrum of oxidized fuel No. 16581

Figure 10. Differential infrared spectrum of fuel No. 16581

8

a. at 3400 cm^{-1}
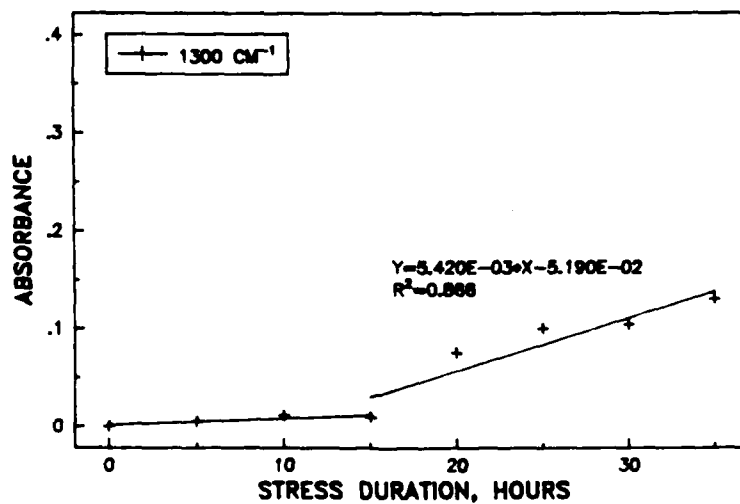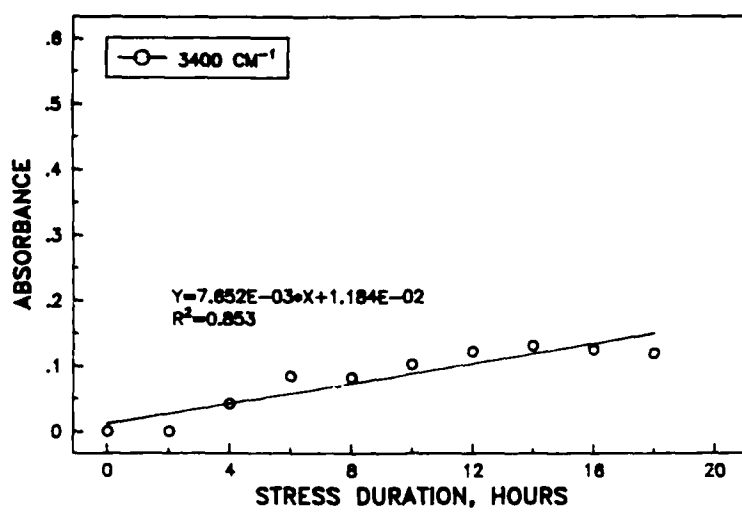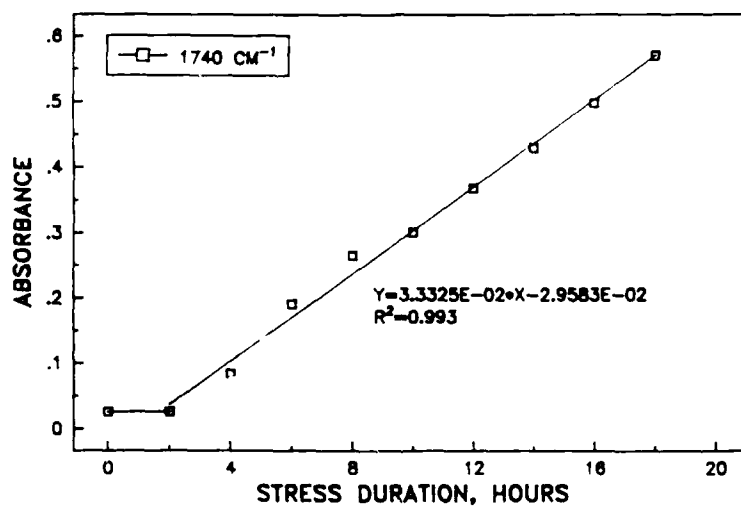

b. at 1740 cm^{-1}

c. at 1300 cm^{-1}

Figure 11. Oxidation of fuel No. 15708 at 100°C/240 kPa

9
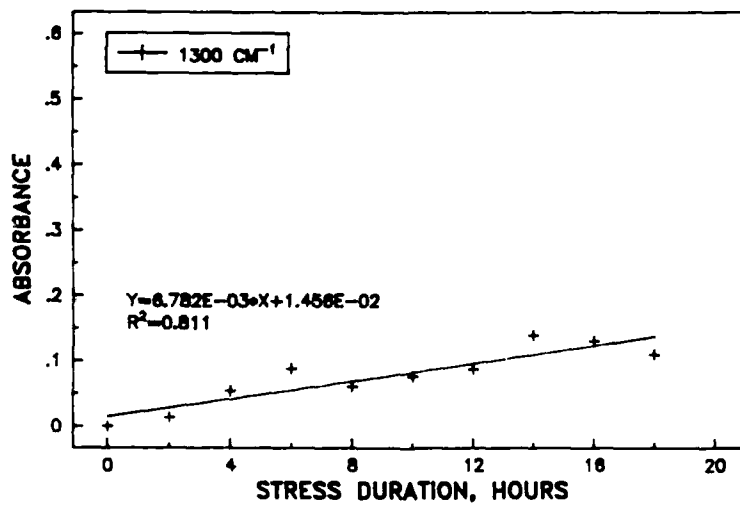
Figure 12. Oxidation of Fuel No. 15708 at 120°C/240 kPa

a. at 3400 cm^{-1}

$Y=7.652E{-}03{*}X+1.184E{-}02$
$R^2=0.853$

b. at 1740 cm^{-1}

$Y=3.3325E{-}02{*}X-2.9583E{-}02$
$R^2=0.993$

c. at 1300 cm^{-1}

$Y=6.782E{-}03{*}X+1.456E{-}02$
$R^2=0.811$
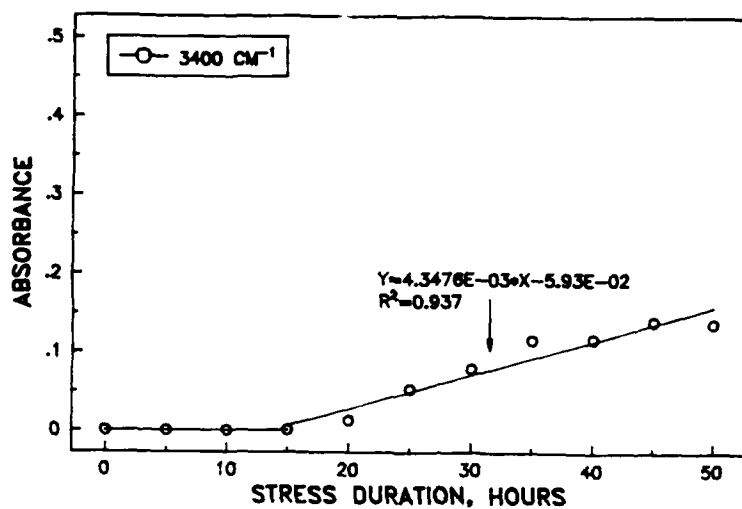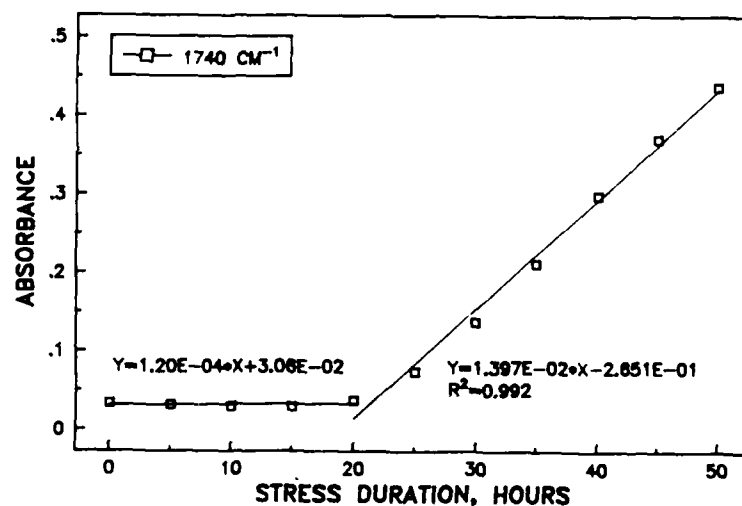
a. at 3400 cm^{-1}
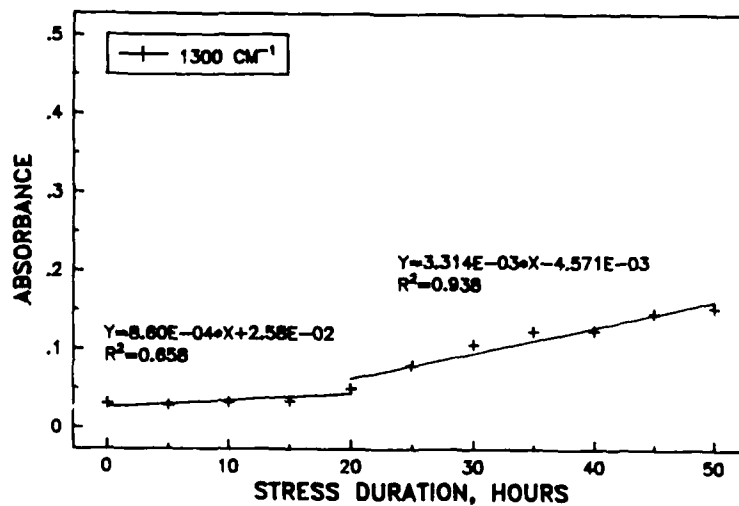
b. at 1740 cm^{-1}

c. at 1300 cm^{-1}

Figure 13. Oxidation of fuel No. 16581 at 100°C/240 kPa

11
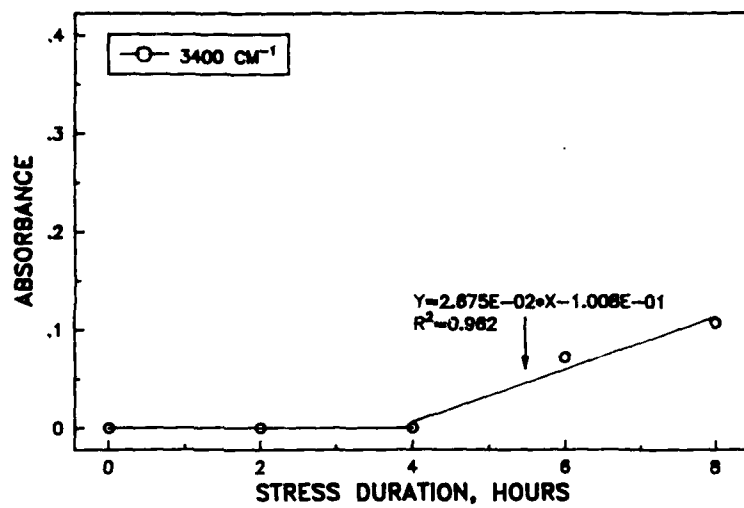
a. at 3400 cm^{-1}
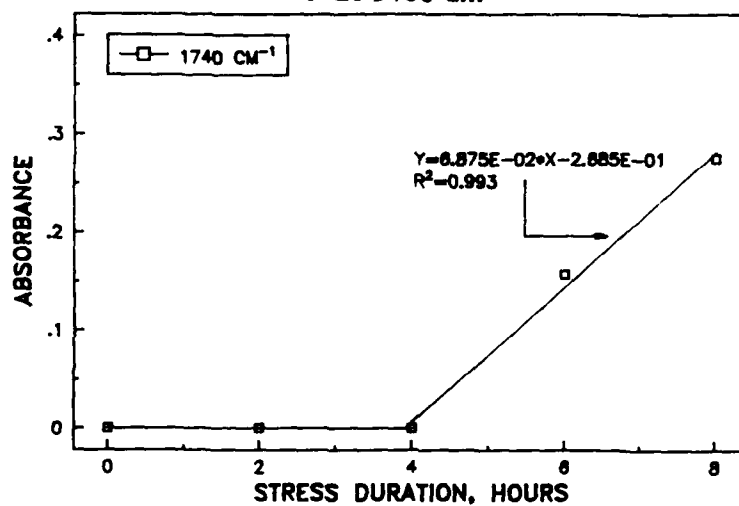
b. at 1740 cm^{-1}
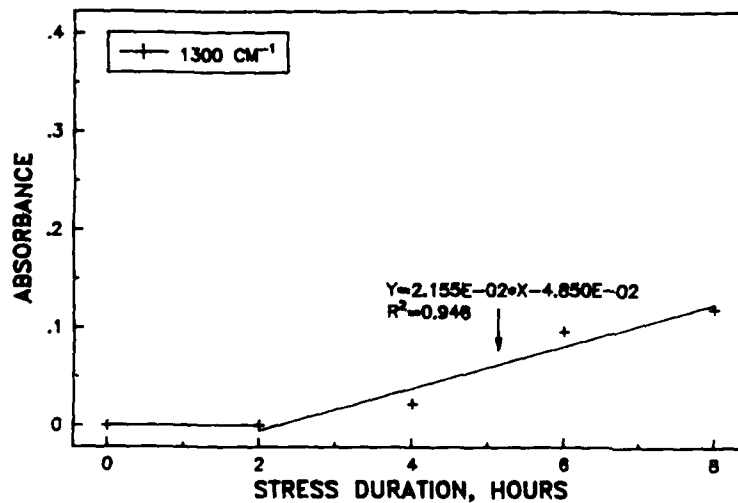
c. at 1300 cm^{-1}

Figure 14. Oxidation of fuel No. 16581 at 120°C/240 kPa

12

at 120°C are shown in Fig. 12, and similar data for fuel No. 16581 are shown in Figs. 13 and 14.

No direct correlation could be found between peroxide concentrations and infrared absorbance results. A comparison of the peroxide and infrared data shows that, for a given temperature and fuel, the infrared data "lag" behind the corresponding peroxide data. For instance, comparisons of Fig. 3 with Fig. 13 show the differences that may be noted in the oxidation of fuel No. 16581 at 100°C as measured by peroxide concentrations and the respective infrared absorbances. While Fig. 3 indicates an induction period of about 10 hours, Fig. 13 depicts an induction period of between 15 and 20 hours.

More consistent and stronger infrared data were obtained at the band centered around 1740 cm^{-1} than at the other frequencies examined. For these reasons, this band was selected to prepare a cursory Arrhenius plot, shown in Fig. 15. This figure illustrates data obtained at 100° and 120°C for the post-induction periods of both fuels. While only a rough estimate may be made using the two available data points, it may be noted that the activation energies contradict those obtained from the peroxide data. This reversal of the order of activation energies may indicate that the infrared absorption at 1740 cm^{-1} is indicative of carbonyl compounds resulting from peroxide decomposition rather
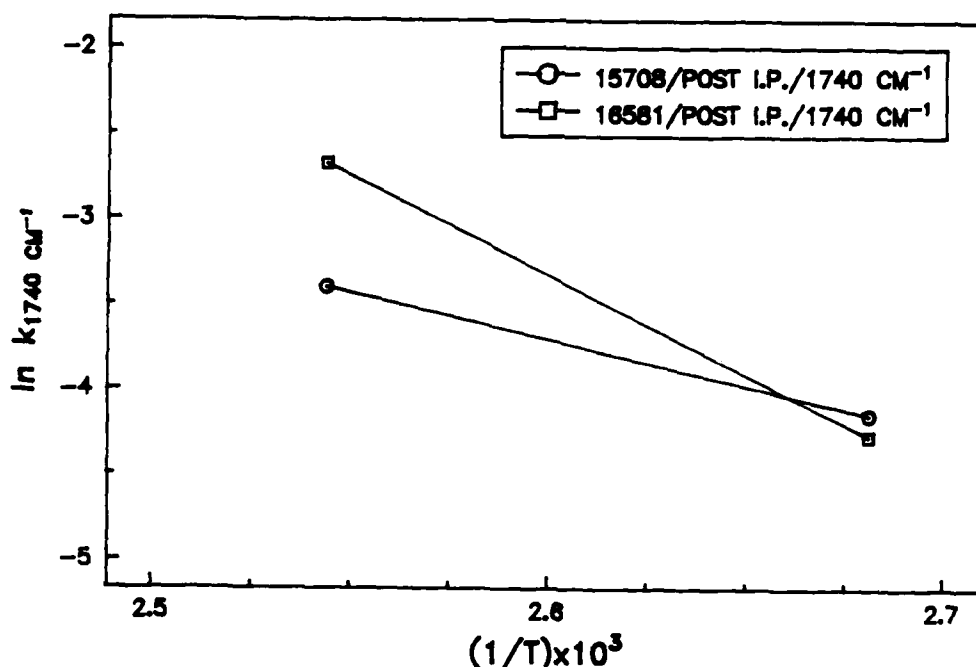

Figure 15. Arrhenius plot of fuel Nos. 15708 and 16581 oxidation (infrared data)

13

than the peroxide itself. This argument may also explain the previously mentioned "lag" that was observed in comparing data derived from the peroxide concentrations and the three regions of infrared absorbances that were noted in the oxidized fuels.

VII. CONCLUSIONS AND RECOMMENDATIONS

The most expedient way to follow the autoxidation of turbine fuels appears to be through the measurement of the peroxide concentrations. Ultraviolet and proton nuclear magnetic resonance spectroscopies did not respond to the the changes in the examined fuels. This failure to respond is apparently due to the relatively low sensitivity of these techniques to the trace concentrations of reactive reaction intermediates.

Preliminary indications are that infrared spectroscopy may be used for the detection and measurement of peroxide decomposition products such as alcohols and carbonyl compounds. Direct detection and measurement of the primary autoxidation intermediates, that is, peroxides and hydroperoxides, were not feasible by the applied nondestructive analytical methods.

To date, direct measurement of peroxide concentrations seems to offer the most expedient way to follow and predict the peroxidation potential of turbine fuels. Application of infrared and other nondestructive instrumental analytical chemical methodologies may be helpful when investigating the entire area of fuel degradation. Such investigation should involve not only the initially formed peroxides, but also the decomposition of these products to final fuel degradation products.

VIII. ACKNOWLEDGMENTS

IX. REFERENCES

1. Shertzer, R.H., "Aircraft Systems Fleet Support/Organic Peroxides in JP-5 Investigations," Final Report, NAPC-433, 1978.

2. Hazlett, R.N., Hall, J.M., Nowack, C.J. and Craig, L., "Hydroperoxide Formation in Jet Fuels," Proc. of Conference on Long-Term Stabilities of Liquid Fuels, No. B132, Tel Aviv, Israel, July 11-14, 1983.

3. Fodor, G.E. and Naegeli, D.W., "Development of a Test Method to Determine Potential Peroxide Content in Turbine Fuels," Proceedings of the 2nd International Conference on Long-Term Storage Stabilities of Liquid Fuels, pp 632-645, San Antonio, Texas, July 29 through Aug. 1, 1986.

4. Fodor, G.E., Naegeli, D.W., Kohl, K.B. and Cuellar, J.P., Development of a Test Method to Determine Potential Peroxide Content in Turbine Fuels -- Part II," Interim Report BFLRF No. 243, AD A189293, prepared by Belvoir Fuels and Lubricants Research Facility (SwRI), Southwest Research Institute, San Antonio, Texas, June 1987.

5. L.J. Bellamy, "The Infrared Spectra of Complex Molecules" John Wiley and Sons, Inc, New York, 1958.